## 9. Hausübung, Statistische Physik

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## Aufgabe H17 Biopolymer growth (4 Punkte)

Consider the chemical equilibrium of a solution of linear polymers made up of identical units. The basic reaction step attaches one of these units (called a monomer) to a polymer of N units, to form a new polymer of N+1 units. Let  $K_N(\tau)$  denote the equilibrium constant for this reaction.

a. Show from the law of mass action that the concentration of N-mers (i.e. polymers made of N units), denoted by [N], satisfies

$$[N] = \frac{[1]^N}{K_1 K_2 \cdots K_{N-1}}.$$

b. Show from the theory of reactions that for ideal gas conditions,

$$K_N = \frac{n_Q(N)n_Q(1)}{n_Q(N+1)} e^{(F_{N+1}-F_N-F_1)/\tau},$$

where

$$n_Q(N) = \left(\frac{2\pi\hbar^2}{M_N\tau}\right)^{-\frac{3}{2}},$$

and  $M_N$  is the mass of an N-mer molecule and  $F_N$  its free energy.

c. For large N, we may assume  $M_N \simeq M_{N+1}$ . Under this condition, express the concentration ratio [N+1]/[N] at room temperature (T=300 K) when there is zero free energy change in the basic reaction step: that is, if

$$\Delta F := F_{N+1} - F_1 - F_N = 0.$$

Assume [1] =  $10^{26}$  m<sup>-3</sup>, as for amino acid molecules in a bacterial cell [Kittel, Am. J. Phys. **40**, 60 (1972)]. The molecular weight of the monomer is  $3.3 \cdot 10^{-25}$  kg.  $(\hbar \simeq 10^{-34} \text{ m}^2\text{kg/s} \text{ and } k_B \simeq 1.38 \cdot 10^{-23} \text{ m}^2\text{kg/s}^2\text{K.})$ 

d. Show that, in order for the reaction to favor large polymers, we would need that, for large N,  $\Delta F < -0.4$  eV approximately.

## Aufgabe H18 Gas-solid equilibrium (8 Punkte)

We want to model two coexisting phases in thermal, diffusive and mechanical equilibrium. We assume that one phase consists of a classical ideal gas. Normally, a solid phase would result from inter-particle interactions. But in order to simplify the problem, we assume that instead the particles have the choice between being totally free (and hence part of the ideal gas, in three dimensional space), or instead attached to a harmonic potential of proper frequency  $\omega$ , with three degrees of freedom. We assume that a particle gets an energy discount of  $-\epsilon_0$  if it accepts to be bound. Also we assume the particles have no internal degrees of freedom. We assume that when free, the particles can wander in a cube of volume  $V = L^3$ , therefore neglecting the volume occupied by the bound particles. One must assume that the particles are distinguishable as oscillators in the solid phase, although not as free particles.

- a. Compute the Gibbs sum for both phases independently.
- b. Express the expected number of particle in each phase as function of the fugacity  $\lambda$ .
- c. Using the results of point (b), and under the assumption that there is a large number of particles in the solid phase, express the pressure of the gas as a function of the temperature and of the external constant parameters M,  $\epsilon_0$  and  $\omega$ .

Hint: In point (b) you have obtained two different expressions for  $\lambda$ . Equate them to obtain an equation which does not involve  $\lambda$ .

d. In the high temperature limit  $\tau \gg \hbar \omega$ , compute the latent heat L using the Clausius-Clapeyron equation. Show that

$$L \simeq \epsilon_0 - \frac{\tau}{2}$$
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